Polymer Bulletin 17, 127–134 (1987)

Polymer Bulletin

Radical polymerization of methyl methacrylate with methyl 2,2-dimethyl-3,3-diphenyl-3-cyanopropionate as a thermal iniferter

Toshinori Tazaki and Takayuki Otsu

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka, 558 Japan

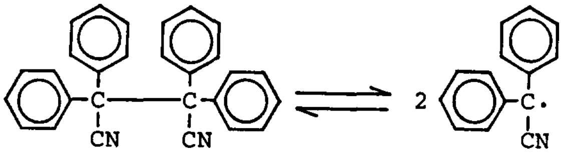
SUMMARY

To clarify the mechanism of living radical polymerization of methyl methacrylate (MMA) with tetraphenylsuccinodinitrile (TPSN) as a thermal iniferter, a model compound for the end group of the poly(MMA) produced, methyl 2,2-dimethyl-3,3-diphenyl-3-cyanopropionate (2), was synthesized and found to initiate a living radical polymerization of MMA, indicating that the hexa-substituted C-C bond in 2 dissociated into radicals. The poly(MMA) thus obtained further initiated the radical polymerization of styrene (St) to give a block copolymer.

INTRODUCTION

In 1982, Otsu and coworkers [1] proposed the concept of iniferter (initiator-transfer agent-terminator) for design of the polymer end structure by radical polymerization. Simultaneously, some iniferters were used to propose a new model for living radical polymerization even in a homogeneous system (see Eq. 2) [2], i.e. both yield and molecular weight of the polymers increase with reaction time. The polymerization of MMA and St with N,N-diethyldithiocarbamate derivatives as photoiniferters [2-10], and of MMA with phenylazotriphenylmethane (PAT) as a thermal iniferter [2,11] were found to proceed via a mechanism close to such living radical polymerization model.

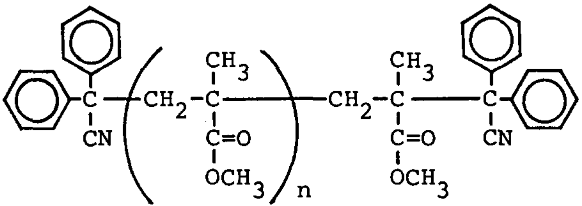
Since 1939, TPSN, one of tetraphenylethane derivatives, has been known to dissociate into two radicals (Eq. 1) which can induce radical polymerization.



TPSN

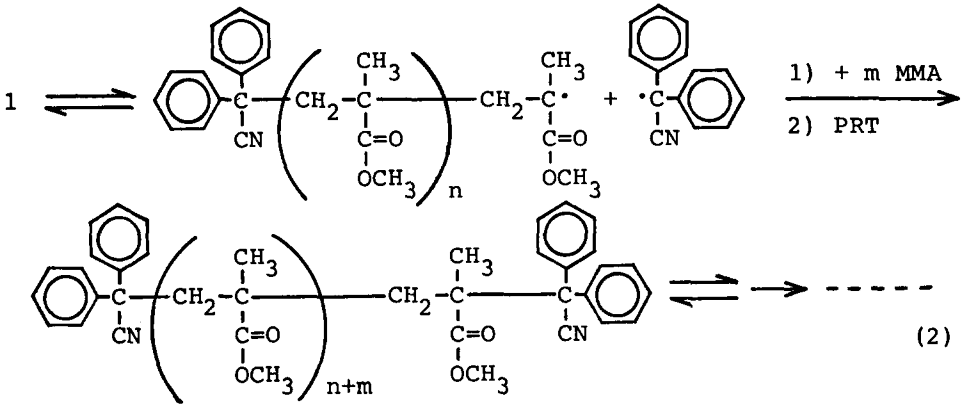
(1)

Since 1981, Braun and coworkers [12-19] have investigated the oligomerization of MMA and its derivatives with 1,2-disubstituted tetraphenylethanes. In these studies using TPSN, Błedzki and Braun [17] isolated the oligomers (1) from the polymerization mixture, and found that their molecular weights increased as a function of reaction time and that they also induced further radical polymerization of MMA.



1 (n= 1.8)

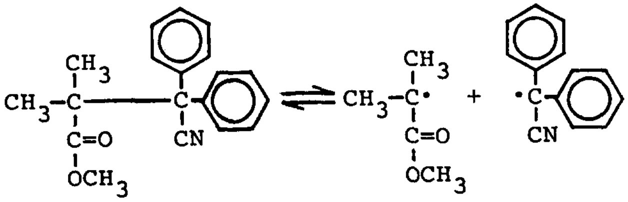
These observations seemed to indicate that the polymerization of MMA with TPSN proceeds via a mechanism close to a living radical polymerization model (Eq. 2) [20] which was proposed by us [2]:



(2)

where PRT is primary radical termination by recombination.

To confirm further this point, a model compound (2) for the end group in 1 was synthesized, and its iniferter activity was examined in order to establish the thermal dissociation of the hexa-substituted C-C bond in 2 (Eq. 3), i.e. the living radical polymerization of MMA with TPSN (Eq. 2) [21]. The results obtained are described in this paper. Recently, Braun and coworkers [18] prepared the same compound and found that it can act as a radical initiator.



2

(3)

EXPERIMENTAL

TPSN was prepared according to the method reported in literature [22,23], and recrystallized from anisole. The model compound (2) was synthesized by the reaction of TPSN with dimethyl 2,2'-azobisisobutyrate in refluxing benzene for 15 hr. After reaction, the benzene was evaporated and the resulting residue was washed well with n-hexane, followed by recrystallization from methanol. Thus, 2 was obtained as a colorless powder: yield, 86%; mp 98 °C (lit. [18] 97 °C). Anal. Calcd. for $C_{19}H_{19}NO_2$: C 77.79; H 6.53; N 4.79%. Found: C 77.11; H 6.58; N 4.55%. ^{1}H-NMR ($CDCl_3$): δ = 1.41(s;6H), 3.58(s;3H), 7.2-7.5(m;10H). MMA, St, 2,2'-azobisisobutyronitrile (AIBN), and solvents were used after purification by ordinary methods.

Polymerization was carried out in a degassed sealed glass tube in a thermostat maintained at 70-100°C. After polymerization for a given time, the content of the tubes was poured into a large amount of methanol to precipitate the polymer. The yield was determined from the weight of the polymer dried. Block copolymerization was also performed similarly. The resulting block copolymer was separated from the polymer mixture obtained by extracting with suitable solvents, i.e. acetonitrile, cyclohexane, and benzene were used as extracting solvents for the parent homopoly(MMA), homopoly(St), and the block copolymer, respectively.

The intrinsic viscosities, $[\eta]$, of the poly(MMA) were determined in benzene at 30 °C and their average molecular weights ($\bar{M}$) were calculated from the following equation [24];

$$[\eta] = 5.2 \times 10^{-5}\ \bar{M}^{\,0.76}$$

^{1}H-NMR was measured by using a JEOL JNM PS-100 spectrometer in deuterochloroform in the presence of tetramethylsilane as an internal standard.

RESULTS AND DISCUSSION

The model compound (2) was found to induce radical polymerization of MMA in the absence of light at 70-100 °C as same as the result by Braun and coworkers [18]. The observed time-conversion and time-$\bar{M}$ relations are shown in Figures 1 and 2, respectively.

From these figures, both conversion and $\bar{M}$ of the polymers were observed to increase with reaction time. Although the time-$\bar{M}$ relations do not pass the origin and the increase of $\bar{M}$ against reaction time (conversion) is not so large as compared with those using PAT [11], the observed result is taken to suggest that the polymerization of MMA with 2 proceeded via a mechanism close to the living radical model in homogeneous system, as described in Eq. 2. Namely, the hexa-substituted C-C bond in both 2 and the poly(MMA) ends produced can be dissociated thermally into the reactive propagating poly(MMA) radical and the less-reactive diphenylcyanomethyl radical, in

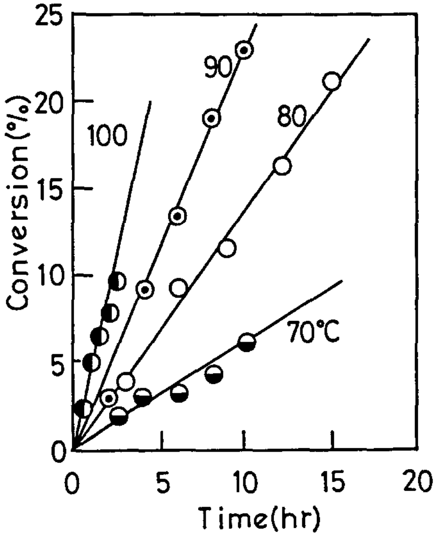


Fig. 1 Time-conversion relations in bulk polymerization of MMA with 2: [2] = 1.0 x 10^{-2} mol/L.

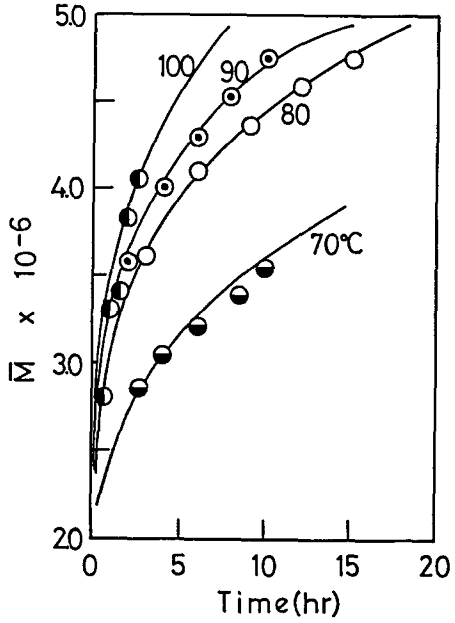


Fig. 2 Time-molecular weight relations in bulk polymerization of MMA with 2: [2] = 1.0 x 10^{-2} mol/L.

which the former induces radical polymerization of MMA and the latter undergoes mainly into PRT by recombination to yield the polymer having the identical end group which can further dissociate into the radicals to react with similar ways.

To clarify further the observed polymerization behavior, some kinetic studies were made. The reaction order of the rate of polymerization with respect to the concentration of 2 was obtained as 0.31 which was identical to that observed for TPSN, indicating that PRT plays an important role in these polymerizations. However, this order was somewhat higher than that (0.25) observed for PAT [11], and it may account for the result that the living nature in radical polymerization of MMA with 2 and TPSN is less prevailing than that with PAT, because PRT is less important (see Eq. 2).

Since the polymerizations of MMA with 2 and TPSN give polymer having a similar end structure, the reactivity of 2 was compared with that of TPSN in bulk polymerization of MMA at 80 °C. The time-conversion and time-$\bar{M}$ (conversion-$\bar{M}$) relations are shown in Figure 3, from which TPSN is more reactive than 2 as a thermal iniferter. It seems to be due to the fact that the radical dissociation of the hexa-substituted C-C bond in TPSN occurs easier than that in 2, as is expected easily from their structures. The increase in $\bar{M}$ against reaction time is low for both iniferters.

As mentioned above, since the poly(MMA) prepared with 2 still has similar hexa-substituted C-C bond at its one chain end, it is expected to act as a polymeric thermal iniferter (i.e. a dormant propagating radical species) of the polymerization of another monomer to provide a AB diblock copolymer. The results of block copolymerization of St are summarized in Table 1.

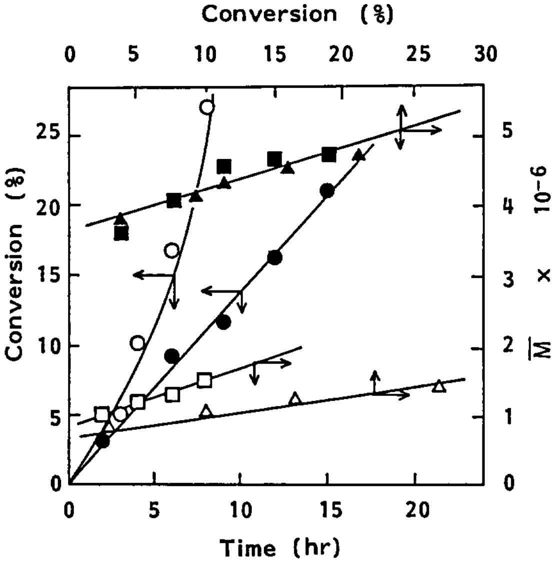


Fig. 3 Time-conversion, time-molecular weight, and conversion-molecular weight relations in bulk polymerization of MMA with TPSN(○, □, △) and 2(●, ■, ▲) at 80°C: [TPSN] = [2] = 1.0 x 10^{-2} mol/L.

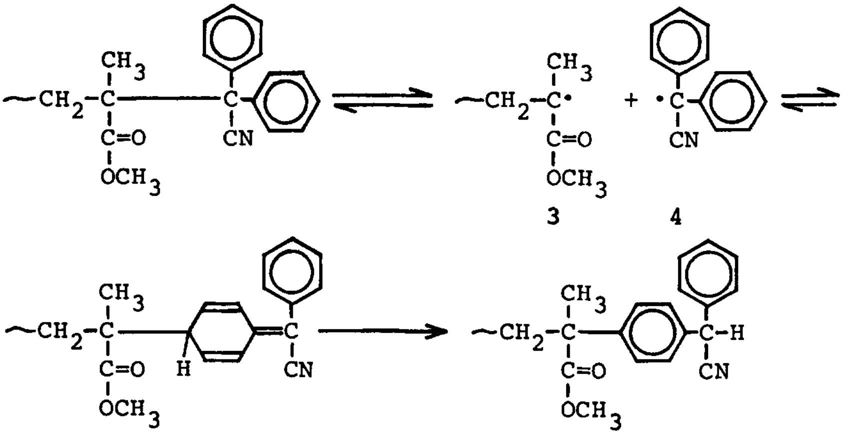
Table 1 Results of Block Copolymerization of St with Poly(MMA) Iniferter Prepared with 2[a)]

Poly(MMA) Iniferter[b)] (g)	Yield (g)	Fractions extracted (%)		
		Homo-poly(MMA)	Homo-poly(St)	Block copolymer
0.30	1.09	19.3	13.0	67.3
0.32	1.33	24.7	14.6	60.7
0.30	2.09	26.6	16.5	56.9
0.30[c)]	1.80	14.9	72.9	12.2

a) Copolymerization conditions: St 10 ml in bulk at 80 °C for 15 hr.
b) Polymerized at 100 °C for 15hr.
c) Polymerized for 20 hr with poly(MMA) prepared with AIBN at 60 °C for 0.8 hr.

From this table, the selectivity of the block copolymer formation is observed to be 56-67%, i.e. 33-44% of the homopolymers is formed.

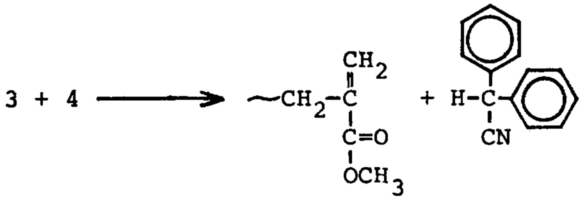
Moreover, the fact that the living nature in this polymerization is not so high (see Figures 2 and 3) as described before, undesirable side reactions (i.e. deactivation reactions of iniferter site) disturbing the ideal living radical polymerization (Eq. 2), might occur during this polymerization.



(4)

The possible side reactions seem to be quite similar to those pointed out for radical polymerization of MMA with PAT [11]. Namely, one of them may be that PRT by disproportionation occurs by radical nuclear-substitution of the propagating poly(MMA) radical (3) to the benzene ring of the diphenylcyanomethyl radical (4) (Eq. 4).

Moreover, PRT by disproportionation (Eq. 5) and initiation with 4 seem to be side reactions.



(5)

The other side reactions may be ordinary recombination and disproportionation between the propagating poly(MMA) radicals.

Since the poly(MMA) thus obtained still has dormant active species, which can be dissociated thermally into radicals, at its chain end, it is necessary to stabilize it to be used. The TGA thermograms of the poly(MMA)s produced with 2 and with AIBN are shown in Figure 4. Therefore, the former was found to decompose easier than the latter, i.e. both of the initial and maximum decomposition temperatures of the former are ca. 40°C lower than the corresponding values of the latter. To deactivate the active end group, the former polymer was refluxed in benzene for 8 hr. Figure 4 also shows the TGA thermogram of the resulting polymer which is quite identical to that observed for the latter polymer, indicating that the dormant active end group was destroyed.

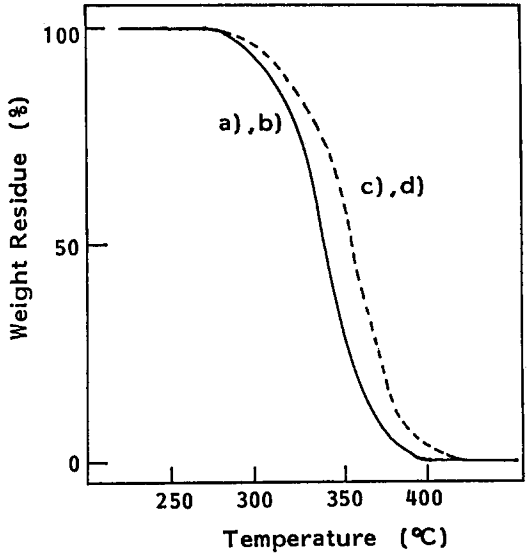


Fig. 4 TGA curves of poly(MMA)s;
a) prepared with TPSN in bulk at 80°C; [TPSN] = 1.0×10^{-2} mol/L
b) prepared with 2 in bulk at 80°C; [2] = 1.0×10^{-2} mol/L
c) prepared with AIBN in bulk at 60°C; [AIBN] = 1.0×10^{-2} mol/L
d) a) or b) heated in benzene at 80°C

ACKNOWLEDGEMENTS

This work is partially supported by a Grant-in-Aid for Developmental Scientific Research from the Ministry of Education, Science and Culture, Japan.

REFERENCES

1. T. Otsu and M. Yoshida, Makromol. Chem., Rapid Commun. 3, 129 (1982).
2. T. Otsu, M. Yoshida and T. Tazaki, Makromol. Chem., Rapid Commun. 3, 133 (1982).
3. T. Otsu, M. Yoshida and A. Kuriyama, Polym. Bull., 7, 45 (1982).
4. T. Otsu and M. Yoshida, Polym. Bull., 7, 197 (1982).
5. T. Otsu, A. Kuriyama and M. Yoshida, Kobunshi Ronbunshu, 40, 583 (1983).
6. T. Otsu and A. Kuriyama, Polym. Bull., **11**, 135 (1984).
7. T. Otsu and A. Kuriyama, J. Macromol. Sci.-Chem., **A21**, 961 (1984).
8. A. Kuriyama and T. Otsu, Polym. J., **16**, 511 (1985).

9. T. Otsu and A. Kuriyama, Polym. J., **17**, 97 (1985).
10. T. Otsu, K. Yamashita and K. Tsuda, Macromolecules, **19**, 287 (1986).
11. T. Otsu and T. Tazaki, Polym. Bull., **16**, 277 (1986).
12. A. Błedzki and D. Braun, Makromol. Chem., **182**, 1047 (1981).
13. A. Błedzki, H. Balard and D. Braun, Makromol. Chem., **182**, 1057 (1981).
14. H. Balard, A. Błedzki and D. Braun, Makromol. Chem., **182**, 1063 (1981).
15. A. Błedzki, H. Balard and D. Braun, Makromol. Chem., **182**, 3195 (1981).
16. A. Błedzki, D. Braun, W. Menzel and K. Titzschkau, Makromol. Chem., **184**, 287 (1983).
17. A. Błedzki, D. Braun and K. Titzschkau, Makromol. Chem., **184**, 745 (1983).
18. A. Błedzki, D. Braun and H. Tretner, Makromol. Chem., **186**, 2491 (1985).
19. A. Błedzki and D. Braun, Polym. Bull., **16**, 19 (1986).
20. T. Otsu, A. Matsumoto and T. Tazaki, Mem. Fac. Eng., Osaka City Univ., in press.
21. This paper was presented at the 29th Meeting of the Society of Polymer Science, Japan, Kobe (1983): T. Otsu, T. Tazaki, A. Matsumoto, and B. Yamada, Preprints, p. 12.
22. K. Auwers and V. Mayers, Chem. Ber., 22, 1277 (1889).
23. G. Wittig and W. Hopf, Chem. Ber., **65**, 760 (1932).
24. E. Cohn-Ginsberg, T. G. Fox and H. F. Mason, Polymer, **3**, 97 (1962).

Accepted January 5, 1987 S